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Biodiesel production catalyzed by highly acidic carbonaceous catalysts synthesized via carbonizing lignin in sub- and super-critical ethanol



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ABSTRACT

Carbonaceous acids were synthesized from dealkaline lignin via solvothermal carbonization, pyrolysis and sulfonation. Carbonization of lignin in sub- and super-critical ethanol provided good surface properties with abundant functional groups (2.81 and 1.35 mmol [H⁺]/g) for the subsequent sulfonation to result in high active and stable catalysts for biodiesel production. Both catalysts (E-P400-2-SO₃H and E-260-20-SO₃H carbonized in sub- and super-critical ethanol) had high acid content of 5.35 and 5.05 (mmol [H⁺]/g), respectively. Highest biodiesel yields of 95.4% and 95.5% were obtained from the esterification of oleic acid at 80 °C with E-260-20-SO₃H and E-P400-2-SO₃H, respectively, with 5 cycles for E-260-20-SO₃H (≥81.9% yield) and 3 cycles for E-P400-2-SO₃H (≥84.6% yield). Both catalysts also applied to produce biodiesel from actual plant oils at 220 °C. High biodiesel yields of 90.9% and 93.2% were obtained from *Jatropha* and blended soybean oils with high acid value of 17.2 and 22.1 mg KOH/g, respectively.

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1. Introduction

Compared with currently used fossil fuels, biodiesel derived from edible and non-edible oils is renewable, biodegradable, less polluted, non-toxic and environmental friendly, and gains significant attentions [1–3]. Non-edible oils such as *Jatropha curcas* L. oil are important raw materials for biodiesel production, because they do not compete with land for food production, and are cheap and sustainable [4–6]. Solid catalysts including solid acids [7–10] and solid bases [3,11] are widely studied for biodiesel production because they are less corrosive than liquid acids or liquid bases, produce less liquid pollutants after catalytic reactions and can be easily recycled. For the transformation of *Jatropha* oil, the critical challenge is its high content of free fatty acids (FFAs) that greatly limits the activity and reuse of base catalysts, and brings serious saponification in base-catalyzed reactions [6]. But, solid acid catalysts can solve this problem, as they can catalyze both esterification and transesterification and produce biodiesel directly from high acid value (AV) oils in one step [7].

Lignin is the second-most abundant organic material in the nature after cellulose. It is largely obtained from industrial pulp-

ing process and can be used as feedstock for producing energy, chemicals and fuels [12–14]. Lignin has higher carbon content than carbohydrates that benefits the economics in biochar production. Recently, carbonaceous catalysts from lignin have been studied (Table 1) [4,15–17]. Compared with char from pyrolysis, hydrothermal biochar prepared under relatively mild condition of hot water provides rich oxygen-containing groups [18–20]. Generally, hydrothermal char from carbohydrates (but not from lignin) has regular morphology with well-distributed functional groups [21]. The main reason is that sugars dissolved in hot-compressed water undergo homogeneous carbonization, however lignin decomposes under both heterogeneous and homogeneous conditions with different routes towards polyaromatic hydrochar [15,22,23]. A proper solvent is required for lignin reaction system such as small molecule alcohols that can help to dissolve lignin to limit heterogeneous routes for the production of lignin biochar with better surface properties to load active sites [24,25].

This work aims to produce carbonaceous acids with high acid content from lignin for biodiesel production. Ethanol as solvent was first screened from different alcohols for lignin char production, and further optimized under sub- and super-critical conditions. The yielded char was sulfonated to carbonaceous acids for the production of biodiesel from oleic acid, *Jatropha* oil and blended soybean oils with high AV according to single-factor and orthogonal experimental designs. The carbonaceous acid prepared in this work with

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Table 1
Comparison of activity of carbonaceous acids derived from lignin in this work with previous studies.

Catalyst	Carbonization materials	Synthesis conditions	Acid content		Esterification of oleic acid		Annotation	Ref.
			NaOH titration (mmol [H ⁺]/g)	Calculated by S content (mmol/g)	Reaction conditions	Biodiesel yield (%)		
Carbonaceous solid acid	Kraft lignin	Impregnation: 85% H ₃ PO ₄ , 1 h; Drying: 105 °C, 24 h; Carbonization: N ₂ , 400 °C, 1 h; Sulfonation: 98% H ₂ SO ₄ , 200 °C, 2 h	1.30	2.10	80 °C, 5 h, 12/1 methanol/oil ratio	96.1	3 cycles with biodiesel yield ≥ 93.6%	[4]
Sulfonated catalyst	Dealkaline lignin	Carbonization: hydrothermal, 225 °C, 20 h; Sulfonation: 98% H ₂ SO ₄ , 150 °C, 12 h	–	0.87	–	–	–	[15]
Carbonaceous sulfonic acid	Kraft lignin	Impregnation: 85% H ₃ PO ₄ , 3 h; Drying: 105 °C, 12 h; Carbonization: N ₂ , 550 °C, 3 h; Sulfonation: 98% H ₂ SO ₄ , 200 °C, 10 h	3.46	0.48	80 °C, 7.5 h, 10/1 methanol/oil ratio	88.7	Biodiesel yield < 77% at the second cycle	[16]
Lignin-based solid acid	Pine Klason lignin	Sulfonation: sulfuryl chloride, 50 °C, 5 h	2.22	0.37	–	–	–	[17]
E-260-20-SO ₃ H ^a	Dealkaline lignin	Carbonization: supercritical ethanol, 260 °C, 8.4 MPa, 20 h; Sulfonation: 98% H ₂ SO ₄ , 150 °C, 10 h	5.05	1.41	80 °C, 7 h, 12/1 methanol/oil ratio	95.4	5 cycles with biodiesel yield ≥ 81.9%	This work
E-P400-2-SO ₃ H ^b	Dealkaline lignin	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h; Pyrolysis: N ₂ , 400 °C, 2 h; Sulfonation: 98% H ₂ SO ₄ , 150 °C, 10 h	5.35	1.06	80 °C, 5 h, 15/1 methanol/oil ratio	95.5	3 cycles with biodiesel yield ≥ 84.6%	This work

^a E-260-20-SO₃H obtained after lignin carbonized in ethanol at 260 °C for 20 h, and sulfonation.

^b E-P400-2-SO₃H obtained after lignin carbonized in ethanol at 180 °C for 1 h, pyrolysis at 400 °C for 2 h, and sulfonation.

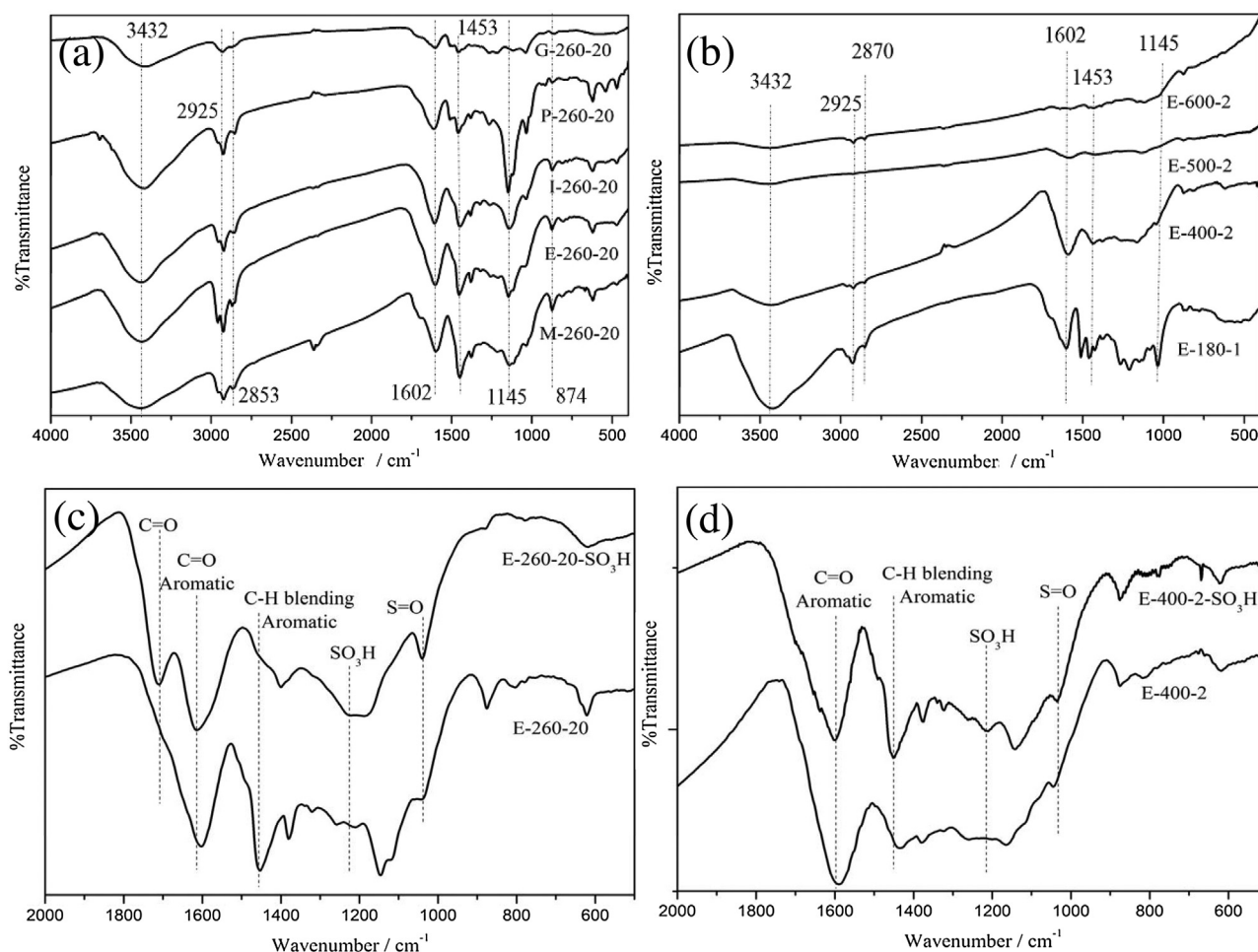


Fig. 1. FT-IR spectra of lignin chars and sulfonated catalysts: (a) biochars carbonized in different alcohols at 260 °C for 20 h, (b) biochars after pyrolysis of E-180-1, (c) sulfonated catalyst of E-260-20, and (d) sulfonated catalyst of E-P400-2.

novel alcohothermal carbonization possessed much higher acid content (5.05–5.35 mmol [H⁺]/g) than those achieved by conventional methods with pyrolysis in previous studies (1.3–3.5 mmol [H⁺]/g) (Table 1) [4,16,17].

2. Material and methods

2.1. Materials

De-alkaline lignin (CAS 9005-53-2) was purchased from J&K scientific Ltd. (Beijing). It was repeatedly washed by distilled water until filtrate's pH reached 4.8 before use. Element composition of washed lignin was C_{56.7}H_{6.6}O_{33.7}S_{2.9}N_{0.2} analyzed by an elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH, Hanau, Germany). Ash content was 3.4% measured by calcination of lignin in air at 600 °C for 2 h in a muffle furnace (4–10, Ever light medical equipment Co., Ltd., Beijing). Reagents dehydrated methanol (>99.5%), iso-propanol (99.0%), 1, 2-propanediol (≥99.97%), glycerol (≥99.0%), H₂SO₄ (≥98.0%), oleic acid (purity of 80% with other fatty acids) were bought from Xilong Chemical Factory Co., Ltd. (Shantou, Guangdong). Dehydrated ethanol (≥99.7%) was purchased from Fengchuan Chemical Reagent Co., Ltd. (Tianjin). Soybean oil (AV of 0.6 mg KOH/g, average molecular weight of 881.1 g/mol) was bought from a supermarket in Kunming, Yunnan (COFCO Corporation, Beijing). It was blended with a certain amount of oleic acid to achieve different AVs (0.6, 6.8, 12.1, 18.2 and 22.1 mg KOH/g with the corresponding average

molecular weights of blended oils of 881.1, 866.2, 863.1, 859.6 and 854.7 g/mol, respectively) for biodiesel synthesis. Two *Jatropha* oil samples were obtained from Yunnan Shenyu New Energy Co., Ltd. (Chuxiong, Yunnan) and Xishuangbanna Tropical Botanical Garden (Menglun, Yunnan) with AVs of 6.3 and 17.2 mg KOH/g and average molecular weights of 862.2 and 860.0 g/mol, respectively.

Methyl esters of [palmitate (C_{16:0}), linolenate (C_{16:1}), stearate (C_{18:0}), oleate (C_{18:1}), linoleate (C_{18:2}), linolenate (C_{18:3}) and heptadecanoic acid (C_{17:0})] with purity ≥99% were obtained from Sigma-Aldrich (Shanghai) as the standards to calibrate biodiesel products in gas chromatography (GC) analysis.

2.2. Alcohothermal carbonization and catalyst preparation

Carbonization of lignin in alcohols was conducted in a Hastelloy (HC-276) autoclave (4596-HPHT, Parr Instrument Co., Moline, IL) with 25 ml volume and 17 ml dead volume. In each experiment, about 16 ml solvent and 0.8 g lignin were added to the autoclave and sealed. After purged by nitrogen (purity of 99.999%), the autoclave with initial N₂ pressure of 5 MPa was heated to 160–260 °C (7.1–9.0 MPa) at heating rate about 11 °C/min, and retained for 0.5–20 h with magnetic stirring (200 rpm) (Table 2). After reactions, the autoclave was powered off and cooled down to room temperature by an electric fan. The solid product was filtered, washed with ethanol and acetone until the filtrate was nearly colorless, freeze-dried (PDU-1200, EYELA, Tokyo Rikakikai Co., Ltd.), grounded and sieved through 200 mesh sieve.

Table 2

Char yield and content of oxygen-containing groups of lignin chars.

No.	Char ^a	Solvent and critical point [26]	Carbonization conditions (Initial N ₂ pressure: 5 MPa)	Char yield (wt%)	Content of oxygen-containing functional groups (mmol [H ⁺]/g)
1	M-260-20	Supercritical methanol; 240 °C and 8.1 MPa	260 °C, 9.0 MPa, 20 h	66.6	0.68
2	E-260-20	Supercritical ethanol; 241 °C and 6.1 MPa	260 °C, 8.4 MPa, 20 h	66.5	1.35
3	I-260-20	Supercritical <i>iso</i> -propanol; 235 °C and 4.8 MPa	260 °C, 8.1 MPa, 20 h	46.3	1.34
4	P-260-20	Subcritical 1,2-propanediol; 352 °C and 6.1 MPa	260 °C, 7.7 MPa, 20 h	3.5	–
5	G-260-20	Subcritical glycerol; 453 °C and 6.7 MPa	260 °C, 7.3 MPa, 20 h	2.7	–
6	E-260-8	Supercritical ethanol	260 °C, 8.4 MPa, 8 h	68.5	1.72
7	E-260-1	Supercritical ethanol	260 °C, 8.4 MPa, 1 h	67.0	2.25
8	E-180-1	Subcritical ethanol	180 °C, 7.8 MPa, 1 h	68.6	2.81
9	E-180-0.5	Subcritical ethanol	180 °C, 7.8 MPa, 0.5 h	56.4	2.76
10	E-160-1	Subcritical ethanol	160 °C, 7.1 MPa, 1 h	72.0	2.73

^a Char was named as “Solvent- carbonization temperature- carbonization time”, and prefix ‘E’, ‘M’, ‘I’, ‘P’ and ‘G’ referred to ethanol, methanol, *iso*-propanol, 1,2-propanediol and glycerol, respectively.

The dried char was named as ‘Solvent- carbonization temperature- carbonization time’, and prefix ‘E’, ‘M’, ‘I’, ‘P’ and ‘G’ referred to ethanol, methanol, *iso*-propanol, 1,2-propanediol and glycerol, respectively. For example, E-180-1 meant that lignin char was carbonized in ethanol at 180 °C for 1 h. Prior to sulfonation, lignin char prepared in subcritical ethanol [critical point (CP): 241 °C and 6.1 MPa] [26] at 180 °C (E-180-1) was further heated to 400, 500 and 600 °C at heating rate of 5 °C/min in a tubular furnace (SGL-1100, Shanghai Daheng Optics and Fine Mechanics Co., Ltd.) under N₂ flow (200 ml/min) and kept for 2 h for pyrolysis. The pyrolyzed char was named as “ ‘E’– ‘P’+ pyrolysis temperature- pyrolysis time”. For example, E-P400-2 meant that lignin char was obtained after carbonization in ethanol at 180 °C for 1 h and pyrolysis at 400 °C for 2 h. Other chars were sulfonated without pyrolysis.

The yield of lignin char was calculated as follows:

$$\text{Char yield (wt\%)} = (\text{weight of char}) / (\text{weight of raw lignin}) \times 100\% \quad (1)$$

Lignin char (1 g) was mixed with 20 ml 98% H₂SO₄ in a 100 ml glass bottle, sealed and put in oil bath at 150 °C for 10 h sulfonation [27]. The sulfonated char was recovered, washed repeatedly with hot distilled water (>80 °C) until the filtrate was neutral, and freeze-dried. The sulfonated catalysts were named as “ ‘E’ – carbonization or ‘P’+ pyrolysis temperature- carbonization or pyrolysis time- SO₃H”. For example, E-260-20-SO₃H meant that lignin char was obtained after carbonization in ethanol at 260 °C for 20 h, and sulfonation. While, E-P400-2-SO₃H meant that lignin char was obtained after carbonization in ethanol at 180 °C for 1 h, pyrolysis at 400 °C for 2 h, and sulfonation.

2.3. Biodiesel production and product analysis

2.3.1. Esterification of oleic acid

Oleic acid, methanol and catalyst with a magnetic bar were loaded in a 50 ml glass bottle sealed by rubber aluminum cap, heated by oil bath under given conditions: temperature (70–90 °C), time (3–7 h), methanol/oil molar ratio (9/1–15/1), catalyst dosage (2.5–7.5 wt%) and magnetic stirring (600 rpm). After reaction, solid catalyst was separated by filtration for recycles.

2.3.2. One step production of biodiesel

Crude *Jatropha* oil (AV of 6.3 and 17.2 mg KOH/g) or blended soybean oil (AV of 0.6–22.1 mg KOH/g) (about 8 g), dehydrated methanol (methanol/oil molar ratio of 12/1) and catalyst (5 wt%

of oil) were added in the Hastelloy autoclave. The autoclave was sealed and pressurized with nitrogen to 5.0 MPa to avoid methanol evaporation and heated to 220 °C and 7.5 MPa within 18–21 min under magnetic stirring (200 rpm). The reaction pressure (7.5 MPa) in the reactor was greater than the saturated vapor pressure (5.8 MPa) [28] of methanol at 220 °C.

2.3.3. Biodiesel analysis

After reaction, liquid phase was filtered (0.22 μm pore size) and dried at 70 °C overnight. Crude biodiesel was collected and analyzed by GC (GC-2014, Shimadzu, Kyoto) equipped with capillary column Rtx-Wax (30 m × Ø0.25 mm × 0.25 μm) under analytical conditions: column temperature of 220 °C, injector temperature of 260 °C, detector temperature of 280 °C, carrier gas of helium, flow rate of 1 ml/min and split ratio of 40/1. Biodiesel yield (weight calculated by GC peaks/actual weight of crude biodiesel × 100%, wt%) was determined by using heptadecanoic acid methyl ester (HDAM; C_{17:0}) as internal standard. The relative response factor of six standard methyl esters [palmitate (C_{16:0}), linolenate (C_{16:1}), stearate (C_{18:0}), oleate (C_{18:1}), linoleate (C_{18:2}) and linolenate (C_{18:3})] to that of HDAM was calibrated as 1.014, 1.023, 1.076, 1.038, 1.019 and 0.926 in previous work [29].

2.4. Catalyst characterization

Morphologies of lignin chars and sulfonated catalysts were examined using scanning electron microscopy (SEM; Quanta 200, Hillsboro, OR). Their specific surface and pore volume were determined by Bruner-Emmett-Teller method (BET; Tristar II 3020, Micromeritics Instrument Co., Ltd., Northcross, GA) with N₂ adsorption. Elemental compositions (C, H, N and S, wt%) were determined by the Vario EL III elemental analyzer. Thermogravimetric analysis (TGA Q5000, TA Instruments, New Castle, DE) was conducted by heating sulfonated catalysts to 800 °C at a heating rate of 10 °C/min with nitrogen flow (75 ml/min). Chemical bonds were analyzed by Fourier transform-infrared spectroscopy (FT-IR; Nexus 670, Nicolet, Waltham, MA). The values of oxygen-containing groups and acid content of samples were determined by NaOH titration. Solid char or catalyst (0.1 g) was mixed with 50 ml NaOH solution (20 mmol/l) and sonicated in an ultrasonic cleaner (AS10200BDT, Tianjin Aote Saiensi Instrument Co., Ltd.) for neutralizing the surface acidity. The consumed base concentration was back-titrated by 20 mmol/l HCl solution using phenolphthalein as indicator [30]. For

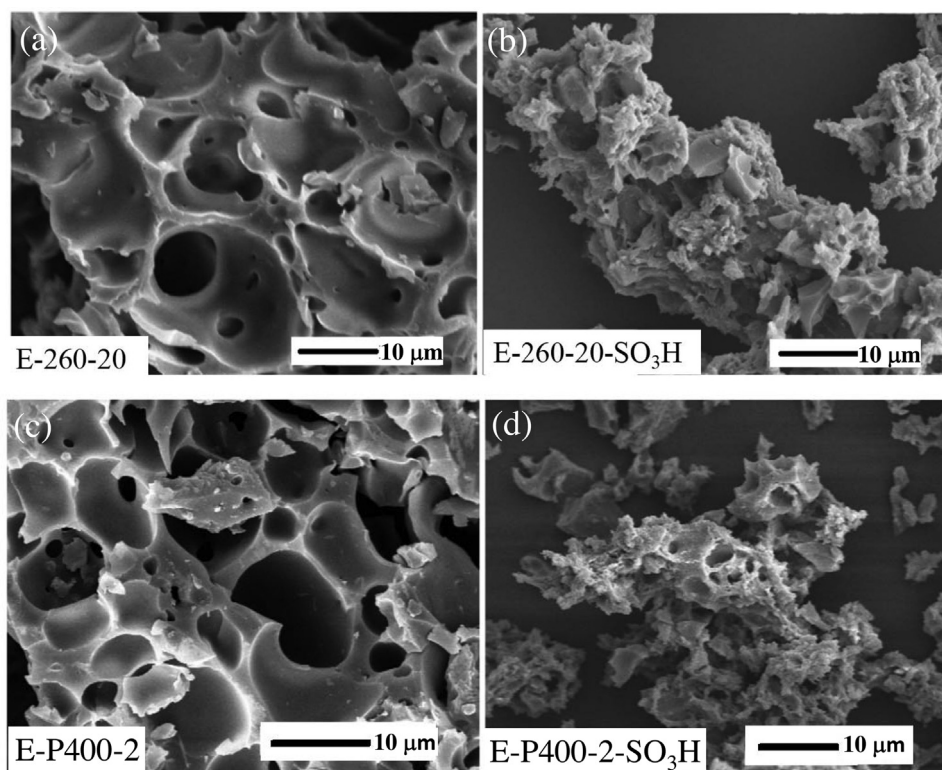


Fig. 2. SEM images of lignin chars and sulfonated catalysts.

carbonaceous acids, oxygen-containing groups are the sole source of acid functionality, so their value is also acid content.

3. Results and discussion

3.1. Alcohothermal carbonization of lignin to biochars

3.1.1. Char yield and element analysis

Carbonization of lignin in different alcohols was studied and results were listed in Table 2. At carbonization temperature of 260 °C and 7.3–9.0 MPa, the order of char yield in different alcohols was methanol \approx ethanol $>$ iso-propanol \gg 1, 2-propanediol \approx glycerol (No. 1–5, Table 2) with the highest char yield ($>66\%$) for methanol and ethanol. It demonstrated that alcohols with shorter carbon chain benefited char formation. The highest C (75.7 wt%) and lowest O (16.0 wt%) contents in ethanol, whereas the lowest C (50.7 wt%) and highest O (40.2 wt%) contents in 1, 2-propanediol were achieved (No. 3 and 5, Table 3). Compared with lignin, C/O and C/H atomic ratio of E-260-20 char increased significantly from 2.24 and 0.73, 6.30 and 1.10, respectively (No. 1 and 3, Table 3), indicating that deoxygenation and reforming reactions deeply occurred in the carbonization of lignin. H/O atomic ratio of lignin (3.08) rose to 5.01 for M-260-20 and 5.72 for E-260-20, respectively (No. 1–3, Table 3), but declined to 2.25 for I-260-20, 1.03 for P-260-20 and 2.71 for G-260-20, respectively (No. 4–6, Table 3). These results illustrated that supercritical methanol [CP: 240 °C and 8.1 MPa] and ethanol [26] had strong chemical reactivity. They took part in the alcohothermal carbonization of lignin, and finally left abundant alkyl functional groups on the surface of biochars. Reaction time had great influence on the carbonization of lignin in supercritical ethanol. The char yield was nearly unchanged with carbonization time of 1, 8 and 20 h (No. 7, 6 and 2, Table 2). However, C/O and H/O ratio of biochars (E-260) greatly increased from 2.72 and 2.79, 6.30 and 5.72, respectively as time prolonged from 1 to 20 h (No. 8 and 3, Table 3), revealing continuous deoxy-

genation of sample and reaction with supercritical ethanol on solid surface.

Carbonization of lignin in subcritical ethanol was also conducted. Biochar yield was 72.0% and 68.6% after carbonization at 160 °C (7.1 MPa) and 180 °C (7.8 MPa) for 1 h, respectively (No. 10 and 8, Table 2), which was slightly higher than that (67% and 66.5%; No. 7 and 2 in Table 2) for E-260-1 and E-260-20 prepared in supercritical ethanol. At 180 °C, biochar yield increased from 56.4% to 68.6% as time rose from 0.5 to 1 h, showing that reaction time had significant influence on lignin carbonization in subcritical ethanol (No. 9 and 8, Table 2). Element analysis illustrated that C/O ratio of chars prepared in subcritical ethanol (2.21 and 2.58 for E-160-1 and E-180-1) was much lower than that (E-260-20) synthesized in supercritical ethanol (6.30) (No. 11 and 9 vs. 3, Table 3). Most oxygen-containing functional groups still remained in these chars (2.7–2.8 mmol $[H^+]/g$ for No. 10 and 8, Table 2). H/O atomic ratio of E-180-1 was 3.21, lower than that (5.72) for E-260-20 and (3.54) E-260-8 but higher than that (2.79) for E-260-1 (No. 9, 3, 7, and 8, Table 3).

3.1.2. Functional groups on lignin chars

Generally, oxygen-containing functional groups are the main active sites of carbonaceous catalysts for surface adsorption and catalytic reactions [31]. Solvent, carbonization temperature and time had significant effect on the amount and distribution of functional groups on the surface of lignin chars [32]. Lignin chars produced in different alcohols had similar IR absorptions but with different intensity (Fig. 1a). They had $-OH$ groups ($3500\text{--}3300\text{ cm}^{-1}$), aliphatic $C-H$ ($3000\text{--}2800\text{ cm}^{-1}$), $C-O$ linkage ($1120\text{--}1050\text{ cm}^{-1}$), as well as benzene skeleton or $C=O$ linkage ($1610\text{--}1600\text{ cm}^{-1}$). Lignin chars produced in supercritical ethanol and methanol contained more saturate alkyl groups as the intensity of absorptions near 2925 and 2853 cm^{-1} was relatively stronger. As discussed before, it could be due to the reaction of supercritical solvents with char surface. By contrast, biochar E-180-1 prepared

Table 3
Elemental compositions of lignin (No. 1), chars (No. 2–14) and sulfonated catalysts (No. 15–20).

No.	Sample ^a	Synthesis conditions	Elemental composition (wt%)				Atomic ratio			
			C	H	O ^b	S	N	C/O	C/H	H/O
1	Lignin	–	56.67	6.55	33.72	2.89	0.17	2.24	0.73	3.08
2	Chars: M-260-20	Carbonization: supercritical methanol, 260 °C, 9.0 MPa, 20 h	72.41	6.10	19.34	2.00	0.15	4.99	1.00	5.01
3	E-260-20	Carbonization: supercritical ethanol, 260 °C, 8.4 MPa, 20 h	75.69	5.77	16.00	2.20	0.34	6.30	1.10	5.72
4	I-260-20	Carbonization: supercritical <i>iso</i> -propanol, 260 °C, 8.1 MPa, 20 h	66.41	3.72	26.25	3.41	0.21	3.37	1.50	2.25
5	P-260-20	Carbonization: subcritical 1,2-propanediol, 260 °C, 7.7 MPa, 20 h	50.72	2.60	40.18	6.22	0.28	1.68	1.64	1.03
6	G-260-20	Carbonization: subcritical glycerol, 260 °C, 7.3 MPa, 20 h	61.29	5.23	30.69	2.49	0.30	2.66	0.98	2.71
7	E-260-8	Carbonization: supercritical ethanol, 260 °C, 8.4 MPa, 8 h	67.60	5.51	24.70	2.01	0.18	3.65	1.03	3.54
8	E-260-1	Carbonization: supercritical ethanol, 260 °C, 8.4 MPa, 1 h	61.91	5.32	30.30	2.19	0.28	2.72	0.98	2.79
9	E-180-1	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h	60.16	6.30	31.12	2.20	0.22	2.58	0.80	3.21
10	E-180-0.5	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 0.5 h	59.02	6.07	32.01	2.72	0.18	2.46	0.82	3.01
11	E-160-1	Carbonization: subcritical ethanol, 160 °C, 7.1 MPa, 1 h	56.80	6.08	34.20	2.67	0.25	2.21	0.78	2.82
12	E-P400-2	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h;	66.60	3.79	28.25	1.10	0.26	3.14	1.47	2.13
13	E-P500-2	Pyrolysis: N ₂ , 400 °C, 2 h	75.40	3.18	19.70	1.50	0.22	5.10	1.99	2.56
14	E-P600-2	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h;	78.80	2.48	16.97	1.41	0.34	6.19	2.67	2.32
15	Catalysts: E-260-20-SO ₃ H	Pyrolysis: N ₂ , 600 °C, 2 h	48.66	2.78	44.01	4.50	0.05	1.47	1.47	1.00
16	E-260-20-SO ₃ H ^c	Carbonization: supercritical ethanol, 260 °C, 8.4 MPa, 20 h;	63.90	5.38	27.05	3.50	0.17	3.15	1.00	3.16
17	E-P400-2-SO ₃ H	Sulfonation: 98% H ₂ SO ₄ , 150 °C, 10 h	64.50	2.71	29.3	3.40	0.09	2.93	2.00	1.47
18	E-P500-2-SO ₃ H	After 5 cycles for biodiesel production	68.77	2.89	24.9	3.21	0.23	3.68	2.00	1.84
19	E-P600-2-SO ₃ H	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h;	70.60	2.01	24.31	2.89	0.19	3.87	2.95	1.31
20	E-P400-2-SO ₃ H ^c	Pyrolysis: N ₂ , 400 °C, 2 h;	63.01	4.70	29.00	2.81	0.48	2.89	1.12	2.57
		Sulfonation: 98% H ₂ SO ₄ , 150 °C, 10 h								
		After 5 cycles for biodiesel production								

^a The alcohothermal char was named as “Solvent- carbonization temperature- carbonization time”, and prefix ‘E’, ‘M’, ‘I’, ‘P’ and ‘G’ referred to ethanol, methanol, *iso*-propanol, 1,2-propanediol and glycerol, respectively. The pyrolyzed char was named as “ ‘E’– ‘P’+ pyrolysis temperature- pyrolysis time”. The sulfonated catalysts were named as “ ‘E’– carbonization or ‘P’+ pyrolysis temperature- carbonization or pyrolysis time- SO₃H”.

^b O (wt%) = 100% – C(%) – H(%) – N(%) – S(%).

^c The catalyst was analyzed after 5 cycles for biodiesel production.

in subcritical ethanol had much weaker aliphatic C–H vibration at 3000–2800 cm^{−1} (Fig. 1b). In addition, strong absorption close to 1145 cm^{−1} observed for lignin char produced in 1, 2-propanediol indicated significant rise in C–O and C–H absorptions.

For chars produced at 260 °C (Table 2, No. 1–5), E-260-20 produced in supercritical ethanol had the highest value of oxygen-containing functional groups [1.35 vs. 1.34 mmol [H⁺]/g for I-260-20 (but only 46.3% char yield) from supercritical *iso*-propanol at 260 °C, 8.1 MPa for 20 h (CP: 235 °C and 4.8 MPa)], with the same value to that synthesized in water at 265 °C for 20 h [21]. At the same

time, it had high char yield 66.5% [slightly lower than 66.6% for M-260-20 (but only 0.68 mmol [H⁺]/g) from supercritical methanol at 260 °C, 9.0 MPa for 20 h]. Therefore, E-260-20 was selected to be sulfonated for biodiesel production in next section. The char (E-180-1) produced in subcritical ethanol at 180 °C for 1 h had the highest value of oxygen-containing functional groups (2.81 mmol [H⁺]/g), so it was also used to be sulfonated after stabilized by pyrolysis at higher temperatures below. After carbonization, S content in P-260-20 char dramatically jumped to 6.22% from 2.89% for lignin (No. 5 vs. 1, Table 3). However, it was not selected to be sulfonated

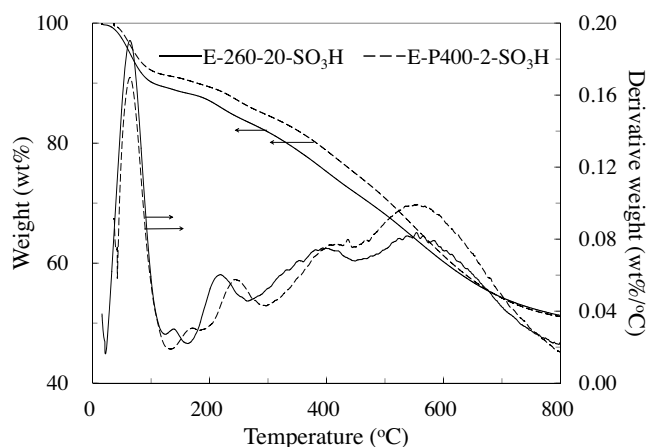
Table 4

Values of oxygen-containing functional groups, BET surface area and pore volume of lignin chars and sulfonated catalysts.

No.	Sample ^a	Synthesis conditions	Content of oxygen-containing functional groups (mmol [H ⁺]/g)	BET surface area (m ² /g)	Pore volume (cm ³ /g)
1	E-260-20	Carbonization: supercritical ethanol, 260 °C, 8.4 MPa, 20 h	1.35	2.3	0.01
2	E-180-1	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h	2.81	ND ^b	ND
3	E-P400-2	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h; Pyrolysis: N ₂ , 400 °C, 2 h	1.47	11.2	0.01
4	E-P500-2	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h; Pyrolysis: N ₂ , 500 °C, 2 h	0.40	271.2	0.13
5	E-P600-2	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h; Pyrolysis: N ₂ , 600 °C, 2 h	0.17	391.7	0.19
6	E-260-20-SO ₃ H	Carbonization: supercritical ethanol, 260 °C, 8.4 MPa, 20 h; Sulfonation: 98% H ₂ SO ₄ , 150 °C, 10 h	5.05	113.1	0.04
7	E-P400-2-SO ₃ H	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h; Pyrolysis: N ₂ , 400 °C, 2 h; Sulfonation: 98% H ₂ SO ₄ , 150 °C, 10 h	5.35	2.7	0.01
8	E-P500-2-SO ₃ H	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h; Pyrolysis: N ₂ , 500 °C, 2 h; Sulfonation: 98% H ₂ SO ₄ , 150 °C, 10 h	–	0.6	ND
9	E-P600-2-SO ₃ H	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h; Pyrolysis: N ₂ , 600 °C, 2 h; Sulfonation: 98% H ₂ SO ₄ , 150 °C, 10 h	–	0.2	ND

^a The synthesized char in hot-compressed ethanol was named as “E– carbonization temperature- carbonization time”. The pyrolyzed char was named as “E– ‘P’+ pyrolysis temperature- pyrolysis time”. The sulfonated catalysts were named as “E– carbonization or ‘P’+ pyrolysis temperature- carbonization or pyrolysis time- SO₃H”.

^b ND: not detected.

**Fig. 3.** Thermal stability (TGA) of sulfonated catalysts.

as catalyst because its char yield was extremely low (3.5%, No. 4, Table 2).

3.1.3. Stabilization of char E-180-1 by pyrolysis

Considering the temperature of 220 °C for biodiesel production from crude *Jatropha* and blended soybean oils, lignin char (E-180-1) obtained at 180 °C in subcritical ethanol needs stabilization at higher temperature (400, 500 and 600 °C) before sulfonation. After pyrolysis, their element compositions and FT-IR spectra were presented in Table 3 and Fig. 1b, respectively. While, the analytical results of functional groups and BET were summarized in Table 4.

In Table 3 (No. 9 vs. 12–14), C increased but O and H declined as pyrolysis temperature rose from 400 to 600 °C because of the dehydration and fracture of chemical linkages at high temperature [19]. C/O ratio of E-P400-2 (3.14) after pyrolysis at 400 °C for 2 h was higher than that of E-180-1 (2.58), but much lower than that of E-260-20 (6.30) prepared in supercritical ethanol at 260 °C for 20 h (No. 12 vs. 9 & 3, Table 3). H/O ratio of E-P400-2 (2.13) was also much lower than that of E-260-20 (5.72) (No. 12 vs. 3, Table 3), which became the most obvious difference between the chars derived in sub- and super-critical ethanol.

Both BET surface area and pore volume of char E-180-1 were too low to be detected. But, after pyrolysis at 400, 500 and 600 °C, the surface area dramatically increased to 11.2, 271.2 and 391.7 m²/g, respectively (Table 4). It was due to the formation of numerous pores in biochars by volatile gases released during pyrolysis at 400–600 °C [18]. High BET surface area means carbon support has a stronger physical adsorption capacity, but it has no direct relationship with the ability of chemical adsorption and catalytic reaction.

FT-IR spectra of char E-180-1 before and after pyrolysis demonstrated that it lost most absorption as pyrolysis temperature rose from 400 to 500 and 600 °C (Fig. 1b). Konwar et al. [33] reported that a large number of functional groups including C–H and C–O linkages were broken and removed when pyrolysis temperature was higher than 500 °C. In Table 4, the total amount of functional groups on lignin char surface dropped obviously from 2.81 to 1.47, 0.40 and 0.17 mmol [H⁺]/g as E-180-1 char pyrolyzed at 400, 500 and 600 °C. However, E-P400-2 char still had more functional groups than that for E-260-20 char (1.47 vs. 1.35 mmol [H⁺]/g, No. 2 in Table 2) prepared in supercritical ethanol at 260 °C.

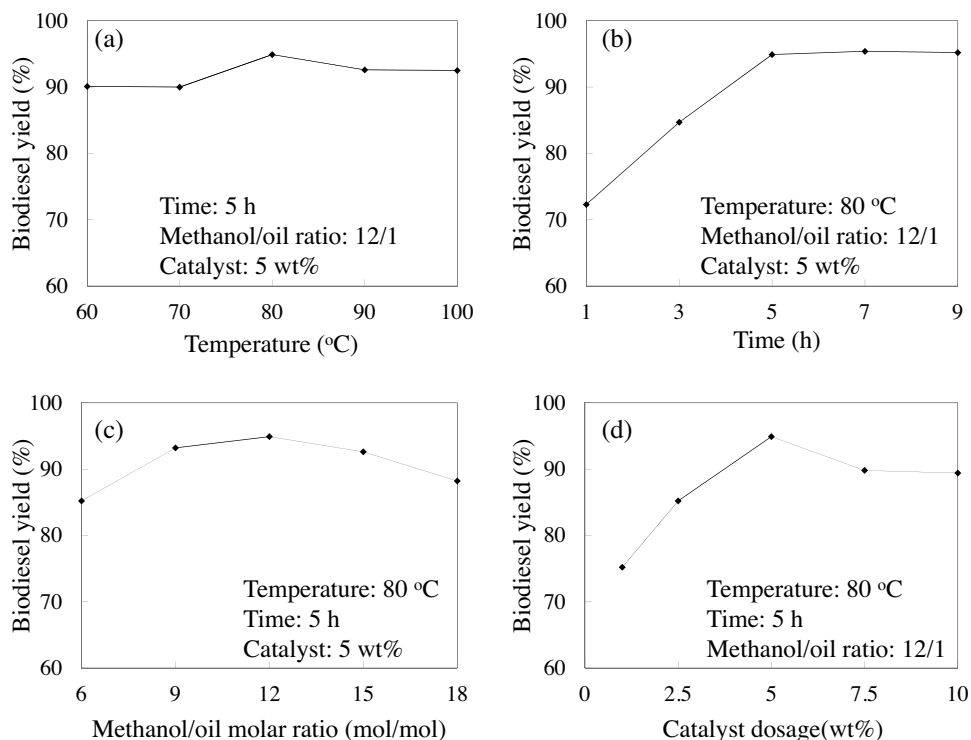


Fig. 4. Effects of variables on esterification of oleic acid with E-260-20-SO₃H catalyst: (a) reaction temperature, (b) reaction time, (c) methanol/oil ratio, and (d) catalyst dosage.

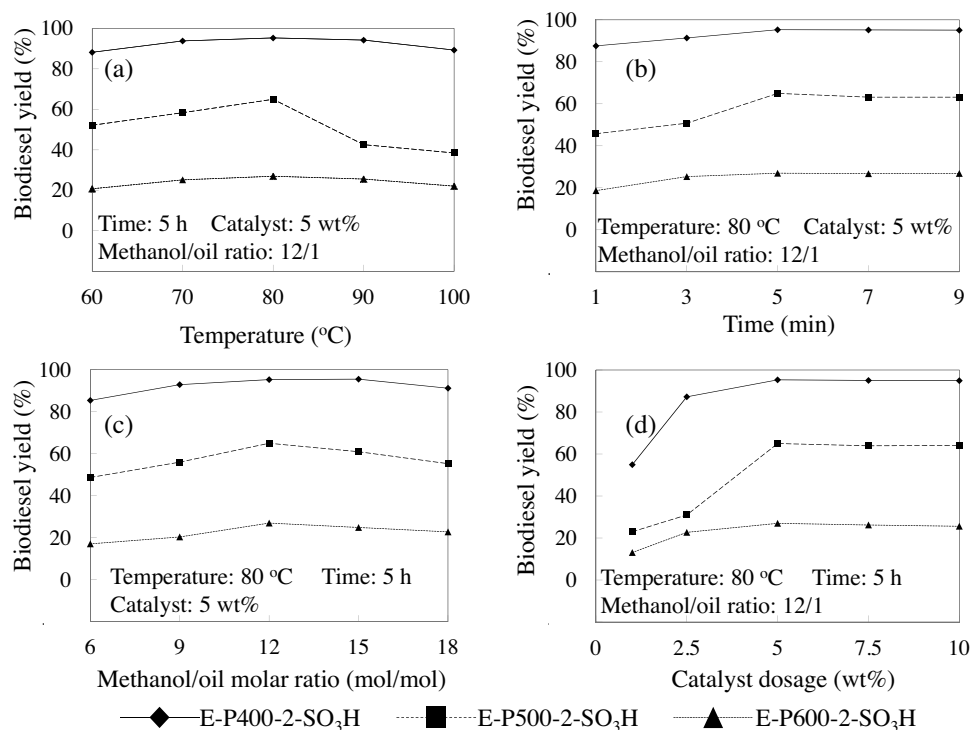


Fig. 5. Effects of variables on esterification of oleic acid with E-P400-2-SO₃H, E-P500-2-SO₃H and E-P600-2-SO₃H catalysts: (a) reaction temperature, (b) reaction time, (c) methanol/oil ratio, and (d) catalyst dosage.

3.2. Characterization of sulfonated catalysts

The amount of acidic oxygen-containing groups of lignin char was less and insufficient to catalyze esterification and transesterification reactions [21]. The order of lignin chars according to their

surface acid group content (mmol [H⁺]/g) was E-P400-2 (1.47) ≈ E-260-20 (1.35) > E-P500-2 (0.40) > E-P600-2 (0.17) (Tables 2 and 4). So, it was necessary to sulfonate lignin chars before use. Element compositions of chars before and after sulfonation were given in Table 3. After sulfonation, S content in char E-260-20 increased

from 2.20 to 4.50 wt% corresponding to sulfonic acid content of 0.69 and 1.40 mmol $\text{SO}_3\text{H/g}$ calculated by S content, respectively. The sulfonated chars obtained in subcritical ethanol contained low S, with sulfonic acid content of 1.06, 1.00 and 0.90 mmol $\text{SO}_3\text{H/g}$ for E-P400-2- SO_3H , E-P500-2- SO_3H and E-P600-2- SO_3H , respectively. However, it should be noted that besides sulfonic acid functional groups, other weak acidic functional groups such as carboxyl and phenolic hydroxyl groups could also contribute to esterification and transesterification [16]. So, the real concentration of total acidic functional groups of sulfonated catalysts was also determined by NaOH titration. Sulfonated chars E-260-20- SO_3H and E-P400-2- SO_3H had acid content of 5.05 and 5.35 mmol $[\text{H}^+]/\text{g}$, respectively, much higher than those reported in previous literatures (Table 1) [4,7,16,34]. By contrast, Li et al. [16] prepared sulfonated carbon by sulfonation of phosphoric acid-activated lignin char by concentrated sulfuric acid at 200°C for 10 h, with acid content of 3.46 mmol $[\text{H}^+]/\text{g}$ by NaOH titration.

FT-IR spectra of sulfonated catalysts E-260-20- SO_3H and E-P400-2- SO_3H were presented in Fig. 1c and d. Absorptions from both $\text{C}=\text{O}$ (1710 cm^{-1}) and $-\text{SO}_3\text{H}$ (1220 and 1040 cm^{-1}) for catalyst E-260-20- SO_3H increased, proving $-\text{SO}_3\text{H}$ groups were loaded on lignin char surface successfully [35]. For catalyst E-P400-2- SO_3H , its absorptions at $\text{C}-\text{H}$ bending (1453 cm^{-1}) and $-\text{SO}_3\text{H}$ (1215 and 1037 cm^{-1}) rose significantly after sulfonation. SEM images (Fig. 2a and c) illustrated that E-260-20 and E-P400-2 chars had a melting-like surface and anomalous pore structure with pore diameter of several micrometers. However, after sulfonation, their surface was etched to be rough (Fig. 2b and d) with particle size shrinking due to strong acid attack [36] and significant reduction in particle size [4].

In Table 4, after sulfonation of E-260-20, its BET surface area increased from 2.3 to $113.1\text{ m}^2/\text{g}$ for catalyst E-260-20- SO_3H because it might be seriously corroded by strong acid. However, BET surface areas of pyrolysis chars were remarkably reduced after sulfonation (2.7, 0.6 and $0.2\text{ m}^2/\text{g}$ for E-P400-2- SO_3H , E-P500-2- SO_3H and E-P600-2- SO_3H , respectively) because numerous micropores over biochar surface might be destroyed and closed by strong acid during sulfonation.

TG curves of the sulfonated catalysts (Fig. 3) showed remarkable weight loss of 11.4 and 9.2 wt% below 150°C due to the removal of adsorbed water, and 6.8 wt% and 6.2 wt% between 150 and 300°C because of the elimination of various oxygen-containing groups for E-260-20- SO_3H and E-P400-2- SO_3H , respectively. It showed that the thermal stability of the catalysts required further improvement for reactions at high temperatures.

3.3. Biodiesel production with sulfonated catalysts

Catalysts produced from both super- and sub-critical ethanol (E-260-20- SO_3H , E-P400-2- SO_3H , E-P500-2- SO_3H and E-P600-2- SO_3H) were applied for biodiesel production in both glass bottles and autoclave according to single-factor and orthogonal designs. All experiments except specially mentioned were repeated twice with deviation (σ) of 0.3–1.1 wt% for esterification, and 0.2–1.2 wt% for both esterification and transesterification of *Jatropha* and blended soybean oils.

3.3.1. Single-factor experiments for esterification of oleic acid

Referred to previous work [4], effects of variables including reaction temperature (60 – 100°C), reaction time (1–9 h), methanol/oil molar ratio (6/1–18/1) and catalyst amount (1–10 wt%) on biodiesel yield were studied, with the results plotted in Figs. 3 and 4. All the experiments were only done once.

In the presence of catalyst E-260-20- SO_3H synthesized in super-critical ethanol (Fig. 4), biodiesel yield greater than 90% was achieved at reaction temperature from 60 to 100°C under the fixed

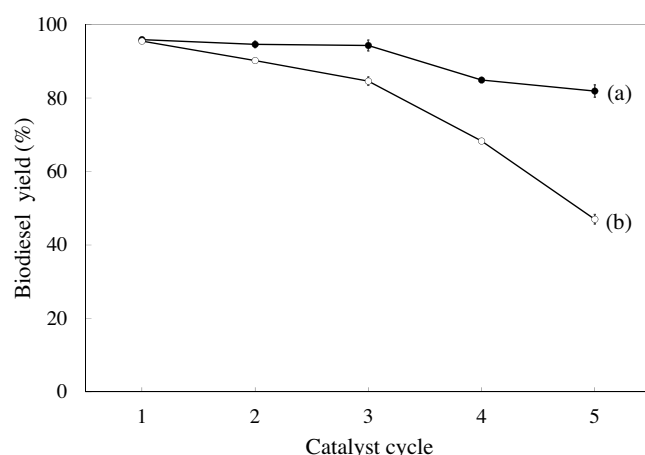


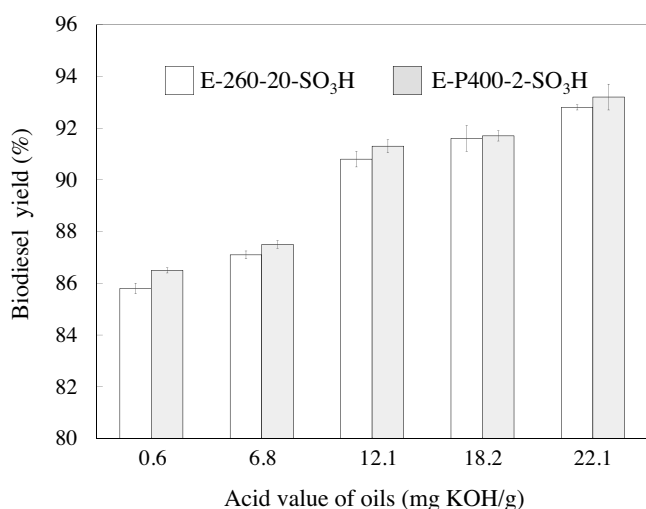
Fig. 6. Catalyst recycles for the esterification of oleic acid: (a) E-260-20- SO_3H catalyst (80°C , 7 h, 12/1 methanol/oil molar ratio, 600 rpm magnetic stirring rate, and 5 wt% catalyst for the first cycle) and (b) E-P400-2- SO_3H catalyst (80°C , 5 h, 15/1 methanol/oil molar ratio, 600 rpm magnetic stirring rate, and 5 wt% catalyst for the first cycle).

initial conditions (time of 5 h, methanol/oil molar ratio of 12/1 and catalyst of 5 wt%), with the highest yield of 94.9% at 80°C (Fig. 4a). Temperature of 80°C was selected to optimize reaction time in Fig. 4b. Under the fixed conditions (80°C , 12/1 methanol/oil molar ratio and 5 wt% catalyst), as time rose from 1 to 5 h, biodiesel yield jumped sharply from 72.3% to the maximum of 94.9%. Biodiesel yield was nearly unchanged from 5 to 9 h because reaction equilibrium of catalytic esterification was realized. Time of 5 h was selected to optimize methanol/oil molar ratio in Fig. 4c. Under the fixed conditions (80°C , 5 h and 5 wt% catalyst), biodiesel yield was first promoted from 85.2% to the highest of 94.9% then declined to 88.2% as methanol/oil molar ratio increased from 6/1 to 12/1 and 18/1. Methanol/oil molar ratio of 12/1 was selected to optimize catalyst dosage in Fig. 4d. The decrease in biodiesel yield with high catalyst amount may be due to the difficult mixing of liquid reactants with high concentration of solid catalyst under magnetic stirring, while the yield decrease at high methanol/oil ratio might be caused by the relative low catalyst concentration with excess methanol [8,34]. Under the fixed conditions (80°C , 5 h and 12/1 methanol/oil molar ratio), biodiesel yield increased then decreased as catalyst grew from 1 to 10 wt%, with the highest yield of 94.9% achieved at 5 wt% catalyst.

Catalysts synthesized in subcritical ethanol at 180°C for 1 h were used to optimize biodiesel production (Fig. 5). Under the fixed conditions (5 h, 12/1 methanol/oil molar ratio and 5 wt% catalyst) (Fig. 5a), as temperature rose from 60 to 80°C , biodiesel yield increased from 88.2% to 95.3% with E-P400-2- SO_3H , from 52.2% to 65.0% with E-P500-2- SO_3H and from 20.8% to 27.0% with E-P600-2- SO_3H , respectively. As temperature rose further to 100°C , Biodiesel yield declined. Temperature of 80°C was selected to optimize reaction time in Fig. 5b, under the fixed conditions (80°C , 12/1 methanol/oil molar ratio and 5 wt% catalyst), as time was prolonged from 1 to 5 h, biodiesel yield increased from 87.6% to 95.3% with E-P400-2- SO_3H , from 45.8% to 65.0% with E-P500-2- SO_3H and from 18.7% to 27.0% with E-P600-2- SO_3H , respectively. As reaction time further rose to 9 h, biodiesel yield seemed promoted little. Time of 5 h was selected to optimize methanol/oil ratio in Fig. 5c. Under the fixed conditions (80°C , 5 h and 5 wt% catalyst), as methanol/oil ratio rose from 6/1 to 12/1, biodiesel yield increased from 85.4% to 95.3% with E-P400-2- SO_3H , from 48.7% to 65.0% with E-P500-2- SO_3H and from 17.1% to 27.0% with E-P600-2- SO_3H , respectively. But, biodiesel yield declined to 91.2%, 55.3% and 22.8%, respectively as the ratio further increased to 18/1. So, methanol/oil ratio of 12/1

Table 5Biodiesel yield for the esterification of oleic acid with E-260-20-SO₃H and E-P400-2-SO₃H catalysts according to an orthogonal design L₉(3)⁴

No.	A Temperature (°C)	B Time (h)	C Methanol/oil (mol/mol)		D Catalyst (wt%)		Biodiesel yield (%) ^a		
							E-260-20-SO ₃ H	E-P400-2-SO ₃ H	
1	70	3		9		2.5		86.2 ± 1.1	57.3 ± 1.7
2	70	5		12		5		92.2 ± 0.6	89.0 ± 1.0
3	70	7		15		7.5		92.9 ± 0.5	87.4 ± 0.9
4	80	3		12		7.5		92.0 ± 0.8	77.6 ± 1.5
5	80	5		15		2.5		93.5 ± 1.0	91.7 ± 1.2
6	80	7		9		5		94.0 ± 0.6	89.7 ± 0.9
7	90	3		15		5		90.6 ± 0.7	80.1 ± 1.1
8	90	5		9		7.5		91.8 ± 1.1	89.8 ± 0.7
9	90	7		12		2.5		93.9 ± 0.9	88.8 ± 1.0
	I ^b	II ^c	I	II	I	II	I	II	
K ₁	90.4	77.9	89.6	71.7	90.7	78.9	91.2	79.3	
K ₂	93.2	86.3	92.5	90.2	92.7	85.1	92.3	86.3	
K ₃	92.1	86.2	93.6	88.6	92.3	86.4	92.2	84.9	
R	2.7	8.4	4.0	18.5	2.0	7.5	1.1	7.0	

^a Biodiesel yield was the average of two duplicate tests.^b 'I' referred to catalyst E-260-20-SO₃H.^c 'II' referred to catalyst E-P400-2-SO₃H.**Fig. 7.** Biodiesel yield of blended soybean oils with different acid values with E-P400-2-SO₃H and E-260-20-SO₃H catalysts (220 °C, 5 h, actual pressure of 7.5 MPa, methanol/oil molar ratio of 12/1, 200 rpm magnetic stirring rate, and 5 wt% catalyst).

was selected as the best value. Similarly, in Fig. 5d, under the fixed conditions (80 °C, 5 h and 12/1 methanol/oil molar ratio), biodiesel yield had the maximum values of 95.3%, 65.0% and 27.0% with the three catalysts, respectively at 5 wt% dosages.

In conclusion, the best reaction conditions are temperature of 80 °C, time of 5 h, methanol/oil molar ratio of 12/1, and catalyst of 5 wt% with best biodiesel yields of 94.9% for E-260-20-SO₃H, 95.3% for E-P400-2-SO₃H, but very low yields of 65.0% for E-P500-2-SO₃H and 27.0% for E-P600-2-SO₃H. It reveals that pyrolysis at high temperatures does not benefit the activity of sulfonated catalysts because of serious abscission of oxygen-containing functional groups of lignin chars (Table 4) and decrease of sulfonic group content (S content remarkably declined, Table 3) during pyrolysis. Therefore, E-260-20-SO₃H and E-P400-2-SO₃H catalysts with high acidity and activity were used further for esterification of oleic acid in the following orthogonal optimization section.

3.3.2. Orthogonal optimization of esterification of oleic acid

Based on the above results, orthogonal design [L₉(3)⁴] with 4 factors and 3 levels [37] was used to optimize biodiesel production from oleic acid with E-260-20-SO₃H and E-P400-2-SO₃H catalysts: reaction temperature (A: 70, 80 and 90 °C), reaction time (B: 3, 5

and 7 h), methanol/oil molar ratio (C: 9/1, 12/1 and 15/1) and catalyst dosage (D: 2.5, 5 and 7.5 wt%) (Table 5). K₁, K₂ and K₃ refer to the average effect of certain factor at the lowest, the moderate and the highest levels, respectively. While R (the abbreviation of term “range” in statistics) is the variation of effect resulted by the change of test level of certain factor. It is determined by the difference between the maximum and minimum values in experimental results [37]. The optimal reaction conditions for E-260-20-SO₃H were A₂B₃C₂D₂ (80 °C, 7 h, 12/1 methanol/oil molar ratio and 5 wt% catalyst) with the highest biodiesel yield of 95.4%. The optimal conditions for E-P400-2-SO₃H were A₂B₂C₃D₂ (80 °C, 5 h, 15/1 methanol/oil molar ratio and 5 wt% catalyst) with biodiesel yield of 95.5%. According to the range analysis, the influence of four factors on biodiesel yield followed the order: reaction time » reaction temperature > methanol/oil molar ratio ≈ catalyst dosage. The results from orthogonal optimization were basically in consistent with the above single-factor tests.

3.3.3. Catalyst cycles

Catalyst cycles were performed under the conditions of 80 °C, 7 h, 12/1 methanol/oil molar ratio and 5 wt% catalyst for E-260-20-SO₃H, and 80 °C, 5 h, 15/1 methanol/oil molar ratio and 5 wt% catalyst for E-P400-2-SO₃H (Fig. 6). E-260-20-SO₃H catalyst was cycled 5 times with biodiesel yields of 95.4%, 94.6%, 91.3%, 84.9% and 81.9%. E-P400-2-SO₃H catalyst was cycled 5 times with biodiesel yields of 95.5%, 90.2%, 84.6%, 68.3% and 47%. So, catalyst synthesized in supercritical ethanol (E-260-20-SO₃H) was more stable.

The decline of catalytic activity might be caused by the leaching of –SO₃H groups in methanol. After 5 cycles, S content decreased from 4.50 to 3.50 wt% (corresponding to sulfonic acid content of 1.41 and 1.09 mmol SO₃H/g) for E-260-20-SO₃H, decreased from 3.40 to 2.81 wt% (corresponding to sulfonic acid content of 1.06 and 0.88 mmol SO₃H/g) for E-P400-2-SO₃H (Table 3). The leaching was supposed mainly from some –SO₃H groups connected to relatively unstable aliphatic groups other than those bonded to arenes with high chemical and thermal stability. Assuming all lost S from solid catalyst (5 wt%) going into product biodiesel, the increased concentration of S in biodiesel would be less than 0.01%, which was comparable to the biodiesel standard of European Union (EN14214, S < 10 mg/kg). High viscous materials remained on the active sites of catalysts were also possibly responsible for the deactivation [6].

The sulfonated lignin catalysts synthesized in super- and sub-critical ethanol in this work was more active and stable than previous reports. Li et al. [16] studies the catalytic esterification of

oleic acid with a sulfonated catalyst from phosphoric acid-activated biochars of industrial alkaline lignin with biodiesel yield of 88.7% at 80 °C, 7.5 h, 10/1 methanol/oil molar ratio and 10 wt% catalyst. The yield decreased to <77% for the second cycle (Table 1). In this work, high biodiesel yields of 95.4% and 81.9% were achieved for the first and fifth catalytic cycle of E-260-20-SO₃H under similar reaction conditions. This might be due to the better surface properties with higher surface acid content of E-260-20-SO₃H and E-P400-2-SO₃H (>5 vs. 3.46 mmol [H⁺]/g, Table 1). The regeneration of solid catalysts can be achieved by proper washing and resulfonation [10].

3.3.4. Biodiesel production from *Jatropha* and blended soybean oils

Both catalysts (E-260-20-SO₃H and E-P400-2-SO₃H) were further used to esterify and transesterify actual plant oils: *Jatropha* and blended soybean oils with high AVs for the production of biodiesel. The reaction conditions were 220 °C, 5 h, 12/1 methanol/oil molar ratio and 5 wt% catalyst, referred to previous work [4].

In Fig. 7, high FFAs benefited biodiesel production from blended soybean oils (with more than 50% triglycerides). As AV of oils rose from 0.6 to 22.1 mg KOH/g, biodiesel yield continuously increased from 85.8% to 92.8% for E-260-20-SO₃H, from 86.5% to 93.2% for E-P400-2-SO₃H. Because esterification was easier proceeded than transesterification catalyzed by acid, which was consistent with previous work [38]. On the other hand, FFAs also catalyzed transesterification. For *Jatropha* oils, E-P400-2-SO₃H presented slightly higher active than E-260-20-SO₃H. Biodiesel yields of *Jatropha* oils were 87.6% and 90.9% with E-P400-2-SO₃H, and 84.5% and 87.7% with E-260-20-SO₃H, at AV of 6.3 and 17.2 mg KOH/g, respectively. Sulfonated lignin carbonaceous acids synthesized in super- and sub-critical ethanol were able to esterify and transesterify non-edible and high AV oils in one pot to biodiesel.

4. Conclusions

Biochars were synthesized from dealkaline lignin in sub- and super-critical alcohols for the production of carbonaceous acids by sulfonation. Two biochars produced by carbonization in sub-critical ethanol (180 °C) and pyrolysis (400 °C) or carbonization in supercritical ethanol (260 °C) were screened with abundant surface oxygen-containing functional groups (2.81 and 1.35 mmol [H⁺]/g) for sulfonation, resulted in carbonaceous acids with high acid content (5.35 and 5.05 mmol [H⁺]/g). Both catalysts were used for catalytic esterification of oleic acid with biodiesel yield >95% and at least 3 cycles (>84% biodiesel yield). The catalysts were further used in the simultaneous esterification and transesterification of plant oils to biodiesel at 220 °C for 5 h. High biodiesel yields of 90.9% and 93.2% were achieved from *Jatropha* and blended soybean oils with high acid value of 17.2 and 22.1 mg KOH/g, respectively.

Acknowledgements

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Corrigendum

Corrigendum to “Biodiesel production catalyzed by highly acidic carbonaceous catalysts synthesized *via* carbonizing lignin in sub- and super-critical ethanol” [Appl. Catal. B: Environ. 190 (2016) 103–114]



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The authors regret to inform that ... the order of the affiliations was published incorrectly. In author names and affiliations, ‘b’ should be ‘a’, and ‘a’ should be ‘b’ (‘a’ is the first affiliation).

Author would like to apologize for the inconvenience caused.

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